

ENHANCED COAL LIQUEFACTION WITH STEAM PRETREATMENT

P.R. Bienkowski, R. Narayan, R.A. Greenkorn and K.C. Chao*

School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

SUMMARY

A two step process for the liquefaction of coal, in a semi-flow micro reactor, was investigated. The process consisted of pretreating coal with low temperature steam, followed by treatment with supercritical steam. The maximum observed conversion of a Wyodak subbituminous coal, using this two step process, was 40 wt% on a moisture and ash free basis (MAF). The 240 °C pretreatment step resulted in a 32% increase over the conversion observed with just a 400 °C treatment. The coal liquid obtained has a number average molecular weight of 325 and a mass average molecular weight of 373, with a narrow molecular weight distribution. The hydrogen and oxygen content of the extract is increased, a significant amount of the oxygen is present as dihydroxyl aromatics. A highly condensed residue of lower hydrogen and oxygen content is obtained which can be of value as a solid fuel.

INTRODUCTION

Recent investigations have led to the observation (1) that in its native unweathered state coal is a reactive material, far from being the inert solid that it is commonly regarded. Extensive hydrogen bonds connect the poly nuclear aromatic cluster to form a semi-permanent macro molecular structure. The structure is particularly fragile in sub-bituminous coals, and may be subject to rupture with mild treatment to dissociate the hydrogen bonds. Graff and Brandes (2) found that carbon conversion to liquids in pyrolysis at 940 °C was raised from 23% to over 50% if the coal was exposed to steam for times less than 30 minutes at temperatures between about 320 and 360 °C. Both pretreatment and pyrolysis were conducted in 50 atm of steam. This result suggests that coal is partially depolymerized by the steam pretreatment, perhaps by the removal of oxygen linkages. If this is indeed the case, improved yields and/or lighter liquids should result if the pretreated coal is liquefied instead of pyrolyzed.

EXPERIMENTAL

Wyodak coal was pretreated and treated with steam in a semi-flow micro reactor at controlled conditions to exclude oxygen. The apparatus is depicted in Figure 1. The main components are a Milton Roy metering pump (29 to 290 cm³/hr) which provides a continuous and constant flow of distilled deoxygenated water to the reactor, a Tecam fluidized sand bath (model SBS-4) controlled with a Leeds and Northrup controller (Electromax III), a Helicoid pressure gauge (0 to 3000 PSIG), an autoclave micro metering valve and a micro reactor equipped with a sheathed thermocouple (see Figure 2).

The feed material was an unweathered subbituminous Wyodak coal provided by EPRI in a water slurry kept in a sealed air-tight barrel (#4171). Table 1 shows the elemental analysis of samples taken from this barrel. Samples A and B were taken from the top and middle of the barrel and were suction dried for use. These were the main feed material. About a 50 gm sample of this material was removed from the barrel and vacuum dried; a sample of this material is reported as sample C. A few reactions were carried out with this material.

The suction dried coal was prepared in a Buchner filter, by applying suction to it for about one hour. The top portion of the material was removed from the filter and thoroughly mixed to insure a homogeneous sample for reaction. The moisture content of this material (≈ 30 wt %) was determined by weighing a sample before and after further drying in a vacuum oven at 45 °C for 6 hours. Duplicate samples were used for moisture determinations.

Suction dried Wyodak coal is paste-like, and is messy to handle. A free-flowing coal powder was obtained for reaction experiments by drying the coal in vacuum under mild heating. The vacuum dried coal was prepared by suction drying in a Buchner funnel over nitrogen; the material was then transferred in a jar filled with nitrogen, to a vacuum oven and dried for 72 hours at 45 °C. The experimental reaction procedure for vacuum dried coal was similar to suction dried coal except that the separate moisture determination of the dried coal was no longer necessary.

To prepare for reaction the oven dried micro reactor (see Figure 2) was weighed and then filled with about 4 gm of wet suction dried coal or 3 gm of vacuum dried coal and reweighed for an accurate determination of the quantity of material charged to the reactor. The charged reactor was fitted into the apparatus upon connecting tubings and fittings. The system was purged of air by flushing with nitrogen. Enough water was pumped from the buret into the reactor to raise the pressure to 50 psia, about 10 to 12 cm³ being required. The reactor was lowered into the sand bath, the pressure adjusted to 750 psia with the aid of the micro metering valve, as water was pumped into the system at 0.4 cm³/min. The steam generated in the heating coil passed through the reactor, was condensed, and collected in an Erlenmeyer flask.

At the termination of an experiment the reactor was removed from the sand bath, and placed in a vacuum oven over night at 45 °C to remove any water. The reactor was then weighed, the contents were removed and placed in a predried and weighed thimble. The reactor was then reweighed, the

change in weight being compared to the weight gain of the thimble.

The coal in the thimble was extracted with toluene for 4 to 6 hours in a Soxhlet apparatus. The thimble was dried over night in a vacuum oven and reweighed to determine the amount of coal extracted. On selected runs the effluent collected in the Erlenmeyer flask was extracted with chloroform and sent to analysis.

The only time the coal sample was exposed to oxygen of the air was during suction drying at ambient temperature. Oxygen was carefully excluded from the reaction system. Feed water to the reactor was deoxygenated by blowing it with nitrogen. From the time of steam pretreatment the reactor remained tightly closed and completely isolated from air until the reactor was cooled down after steam treatment. The only coal that was heated before reaction was that which was vacuum dried at 45 °C. The suction dried coal was never heated.

EXPERIMENTAL RESULTS

Table 2 shows the conversion of Wyodak coal upon pretreatment and treatment with steam at 750 psia. Treatment and pretreatment (if used) steps each lasted 30 minutes. Conversion expresses the fraction of coal that was extracted by the steam from the reactor plus the fraction that was extracted by toluene from the Soxhlet apparatus. The toluene extraction was small, ranging from 0% to less than 3% of the total reported conversion. Toluene extraction was incorporated in our experimental procedure in order to put our experimental results on the same basis with those of other investigators (3,4,5,6) who wash their coal residue with toluene.

With suction dried coal, when not pretreated, treatment with steam at 200 °C gives a practically zero (2.2%) conversion. Raising the treatment temperature to 400 °C raises the conversion to 30.5%. Pretreatment with steam at 200 °C further raises the conversion to 38.5%. Raising the pretreatment temperature to 240 °C raises the conversion to 40.3%. This is the highest conversion observed in this work, for, upon raising the pretreatment temperature to 320 °C conversion is lowered to 33.8%. Raising the treatment temperature to 430 °C further lowers the conversion to 34.2%.

The conversion of vacuum dried coal is reported in the second part of Table 2, and is generally lower than the corresponding results for suction dried coal. Even the mild heating at 45 °C during vacuum drying made the coal more refractory. Comparison of the results obtained with the two different coal samples convinced us to stop using vacuum dried coal. All other experiments reported here used suction dried coal.

The conversions reported in Table 2 were obtained with 750 psia steam for both the pretreatment and treatment. The effect of steam pressure at the treatment stage was investigated, the results are reported in Table 3. Holding the pretreatment pressure constant at 750 psi, an increase in treatment pressure from 750 to 2500 psia, produced a slight reduction in the observed conversion. Higher pressure apparently increases the rate of retrograde reactions. This effect more than compensates for any increase

in solvent power of the steam at a higher pressure, leading to reduced extraction.

Twenty five experiments were performed in all. The conversions in Tables 3 and 3 represent average values for experiments at the same conditions.

CHEMISTRY

Extract and residue samples from two experiments, Runs 5 and 27, were analyzed by infrared spectroscopy, NMR and FIMS. Run 5 consisted of a 320 °C pretreatment followed by a 430 °C treatment, while Run 27 was at 200 °C and 400 °C.

Table 4 shows the elemental analyses of the extract and the residue of Run 27. The analysis of the feed coal is also shown for comparison. The extract has a higher H/C ratio (1.28) as compared to the feed coal (0.95), whereas the residue has a lower ratio (0.68). The O/C ratio follows a similar pattern, being higher in the extract (0.32) than in the feed (0.28), and lower in the residue (0.13).

The steam pretreatment/extraction process produces a hydrogen-rich extract which contains oxygenated compounds and heteroatomic species of the original coal, leaving behind a more condensed aromatic residue.

The same trend is indicated for nitrogen and sulfur, being enriched in the extract and reduced in the residue. But here because of the small amounts, especially of nitrogen, accuracy is low.

The infrared spectrum of the steam extract of Run 27 is shown in Figure 3. The IR spectrum is dominated by broad, strong -OH stretching vibrations in the 3400-3100 cm^{-1} region. The presence of sharp aliphatic -OH bands just below 3000 cm^{-1} suggests that the extract contains aliphatic material, and reinforces the observed enrichment of H and O in the extract.

Further confirmation is provided by the ^1H NMR spectrum of the steam extract from Run 5 shown in Figure 4. The ratio of $\text{H}_{\text{sat}}/\text{H}_{\text{sat}}$ is 1:30. 43% of the H_{sat} hydrogens are associated with methylene, methine, or methyl groups which are not directly bonded to aromatic nuclei. Another 20% of the H_{sat} appearing as a group of signals in the 2-3 ppm region are associated with hydroaromatic structures or associated with methyl, methylene and methine groups directly attached to an aromatic nucleus. The dominant sharp signal at 1.2 ppm is characteristic of long chain polymethylene groups. Thus, one of the major constituents of the hydrogen rich extract is aliphatics present primarily as long chain polymethylenes, either as free species or attached to aromatic/hydroaromatic ring systems.

The ^{13}C NMR spectrum (Figure 5) is dominated by a number of well resolved lines riding on a spectral envelope in the 15-80 ppm region which is the normal chemical shift region for aliphatic compounds, supporting the presence of significant quantities of aliphatic materials in the steam extract. The most intense signal is at 30.2 which is generally assigned to the internal methylene carbons ($\text{C}_1\text{-C}_2\text{-C}_3\text{-C}_n$) of straight chain alkanes corroborating the presence of long chain polymethylene groups (minimum average carbon chain length; $n_c \sim 8\text{-}10$) which may or may not be attached to an

aromatic ring.

The group of signals in the 15-20 ppm region is probably due to the methylene carbons attached to aromatic rings. The presence of a broad spectral envelope in addition to the sharp alkane lines demonstrate the extract's complexity. The spectral complexity is due to the presence of small amounts of polymethylene type compounds. The complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species. Interestingly, a small, but distinctive signal occurs at 179 ppm which is where the carbonyl carbon of a -COOH group appears suggesting the presence of some carboxylic acids in the extract.

Field ionization mass spectrometry (FIMS) is a mass spectrometry technique which uses a soft ionization mode and allows most molecules to be observed as unfragmented molecular ions. The method can provide a true molecular weight profile for any given complex mixture. Figure 6 represents the field ionization mass spectrum of the extract. The extract has a very narrow molecular weight distribution with number average (M_n) and weight average (M_w) molecular weight of 315 and 373, respectively. Since 75% of the material was volatilized in the FIMS probe the observed molecular weights are a true representation of the extract and the extract is composed of low molecular weight compounds. The most prominent peaks in the spectrum appear at m/z 110, 124, and 138 and can be assigned to dihydroxyl benzene and its methyl and ethyl analogs, respectively. Surprisingly no prominent peaks due to monohydroxyl benzene (phenol) or its C-1 or C-2 analogs are found. The oxygenated compounds present in the extract are best represented by the class of dihydroxyl benzenes and other dihydroxyl aromatics. There are a number of other prominent peaks in the higher molecular weight range which, in all probability, arise from the polymethylenes attached to an aromatic ring (identified by NMR) but the FIMS analysis does not allow ready identification of these compounds.

The presence of reactive components like the polymethylene species, the dihydroxyl benzenes, and the low molecular weight profile of the extract suggests that the coal is very reactive and not a highly condensed, very large molecular weight, intractable molecule. Self condensation and crosslinking reactions of the dihydroxyl aromatics, alkylation of the activated aromatic rings by the polymethylene species in the coal, are some of the retrogressive reactions that these coals can undergo, under the severe processing conditions generally employed.

Pretreatment with steam, at lower temperatures, allows the breaking of hydrogen bonds, loosening up the coal matrix, and stabilizing some of the reactive components in the coal. When the temperature increases during the supercritical extraction step, many of these reactive molecules can be steam volatilized or steam extracted, escaping the loosened coal matrix structure before undergoing retrogressive reactions. This explanation is supported since the introduction of a low temperature pretreatment step before the supercritical steam extraction leads to a 32% increase in conversion.

The presence of reactive dihydroxyl benzenes in the extract is also supporting evidence. Dihydroxyl aromatics have never been reported as occurring in coal liquids obtained under normal coal processing

conditions generally employed. They cannot survive the severe processing conditions. Small amounts of dihydroxyl aromatics have been obtained in flash or fast pyrolysis conditions. The very rapid heating allows the dihydroxyl aromatics to escape the coal matrix before they can undergo retrogressive reactions.

CONCLUSIONS

The steam pretreatment-extraction process produces enhanced extractan yields. The extract has a high H/C ratio due to the presence of long chain polymethylene compounds which may or may not be attached to aromatic rings. The extract contains significant amounts of oxygenated compounds, some of which are present as dihydroxyl aromatics. A highly condensed residue (low H/C ratio) is obtained which can be attractive as a solid fuel for combustion.

ACKNOWLEDGEMENTS

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TABLE 1

ANALYSIS OF WYODAK COAL

SAMPLE	A Wet	B Wet	C Vacuum Dried
Carbon	59.51	59.72	58.17
Hydrogen	4.79	4.13	4.35
Oxygen	17.90	22.44	18.94
Nitrogen	0.79	0.76	0.63
Chlorine	-	-	-
Sulfur	3.97	2.55	3.07
Ash	13.59	13.47	16.46
TOTAL	99.55	103.07	101.62
BTU/lb	10,614	-	10,141

Analysis of samples was performed by Huffman Laboratory.

TABLE 2

Conversion of Wyodak Coal upon Pretreatment and Treatment with Steam at 750 psig

Pretreatment Temp °C	Treatment Temp °C	% Conversion MAF
Suction dried coal		
None	200	2.2
None	400	30.5
200	400	38.5
210	400	40.3
320	400	33.8
320	430	34.2
Vacuum dried coal		
None	400	27.3
200	400	38.4
240	400	34.0

TABLE 3

Effect of Pressure of Treatment Steam on Conversion

Pretreatment Treatment	Temperature: 200°C Pressure: 750 psia Temperature: 400°C
Pressure of Treatment Steam, psia	% Conversion MAF
750	38.5
1500	38.6
2500	36.9

TABLE 4

Elemental Analysis of Extract, Residue, and Feed of Run 37

Wt %	Extract	Residue	Feed
C	54.21	64.97	59.72
H	5.77	3.69	4.13
O	23.42	11.20	22.44
N	4.08	1.01	0.76
S	4.39	2.75	2.55
Ash	8.04	17.55	13.47
Atomic Ratio			
H/C	1.26	0.69	0.95
O/C	0.32	0.13	0.28

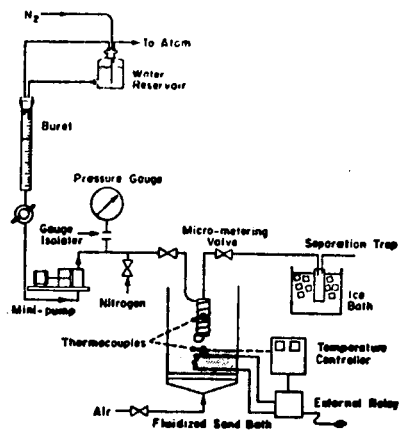


Figure 1: Experimental Apparatus

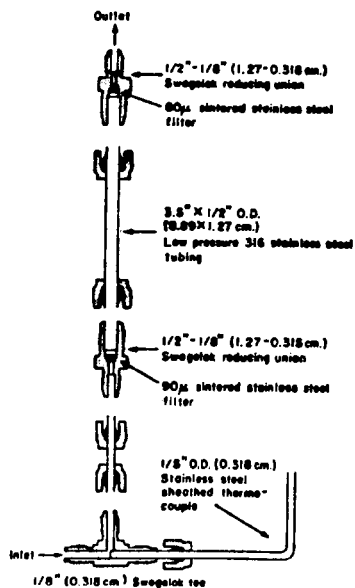


Figure 2: Exploded View of Micro-reactor

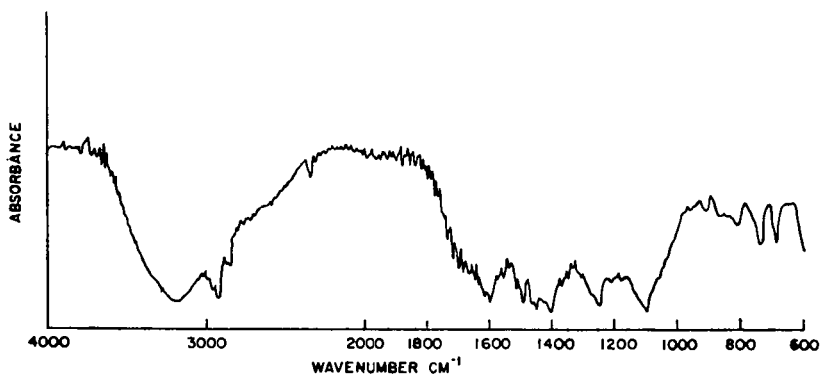


Figure 3: Infrared Spectrum of Steam Extract of Run 27

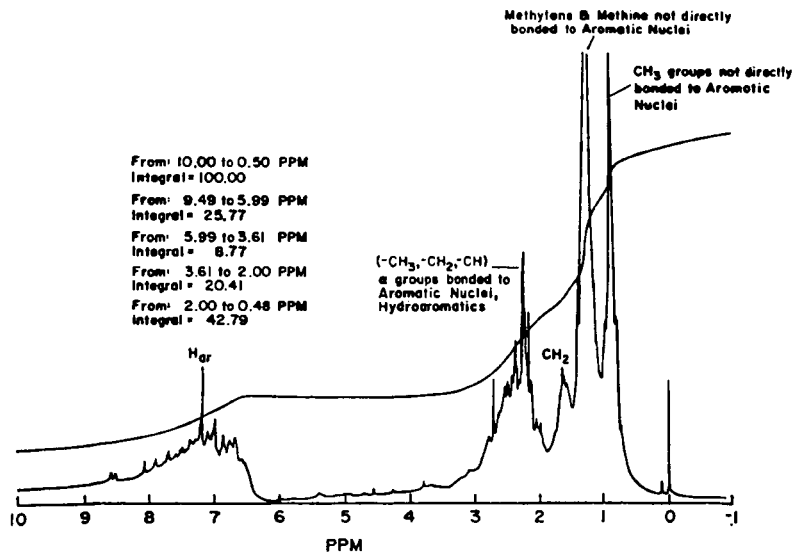


Figure 4: 470 MHz ¹H NMR Spectrum of Steam Extract of Run 5

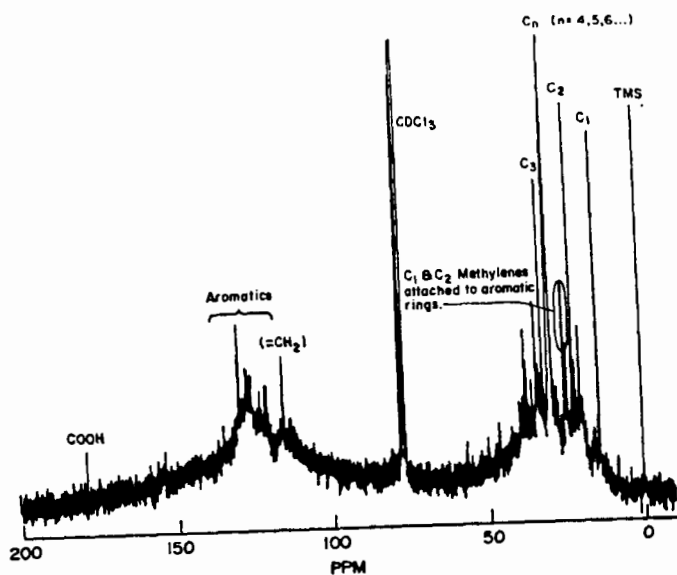


Figure 5: ^{13}C NMR Spectrum of Steam Extract of Run 5

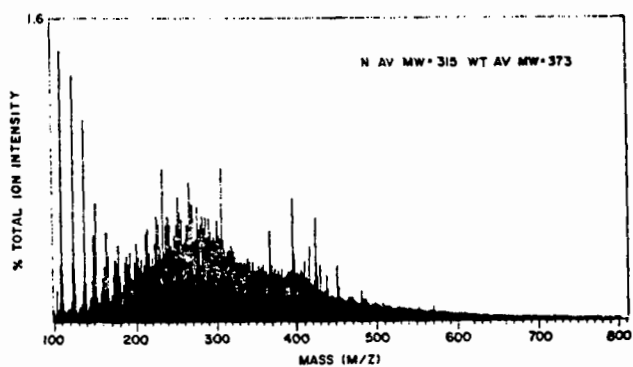


Figure 6: FIMS of Steam Extract of Run 5